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### (54) ELECTROLYTE FOR LITHIUM SECONDARY BATTERY AND MANUFACTURE OF THE LITHIUM SECONDARY BATTERY USING THE SAME

#### (57)Abstract:

PROBLEM TO BE SOLVED: To provide an electrolyte for a lithium secondary battery having high ionic conductivity and good mechanical characteristics.

SOLUTION: An electrolyte for a lithium secondary battery contains at least a composite material of alkoxy modified dialkyl polysiloxane and polyalkylene oxide. The electrolyte for the lithium secondary battery containing at least the composite material of alkoxy modified dialkyl polysiloxane and polyalkylene oxide is impregnated in a nonwoven fabric, gelled, and this impregnated nonwoven fabric is carried between a positive electrode and a negative electrode to manufacture the lithium secondary battery.

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(54) 【発明の名称】 リチウム2次電池用電解質及びこれを用いたリチウム2次電池の製造方法

(57) 【要約】

【課題】 本発明の課題は、優れたイオン伝導性を有し、機械的特性の良好なリチウム2次電池用電解質を提供することにある。

【解決手段】 少なくともアルコキシ変性ジアルキルポリシロキサンとポリアルキレンオキサイドとの複合物を含有することを特徴するリチウム2次電池用電解質。及び少なくともアルコキシ変性ジアルキルポリシロキサンとポリアルキレンオキサイドとの複合物を含有するリチウム2次電池用電解質を不織布に含浸してゲル化した後、正極及び負極材間に担持させることを特徴とするリチウム2次電池の製造方法。

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## 【特許請求の範囲】

【請求項1】 少なくともアルコキシ変性ジアルキルポリシロキサンとポリアルキレンオキサイドとの複合物を含有することを特徴するリチウム2次電池用電解質。

【請求項2】 請求項1に於けるリチウム2次電池用電解質を不織布に含浸してゲル化させた後、正極及び負極材間に担持させることを特徴とするリチウム2次電池の製造方法。

## 【発明の詳細な説明】

【0001】

【発明の属する技術分野】この発明は、リチウム2次電池用電解質、更にはリチウム2次電池の製造方法に関する。

【0002】

【従来の技術】リチウム2次電池は理論エネルギー密度が高く、ポータブル電子機器電源をはじめ、電気自動車、電力貯蔵用電源等その応用範囲は広い。従来のリチウム2次電池に用いられている電解質は、リチウムの高い反応性のためにイオン伝導度の高い水溶液系が使えないことから、リチウム塩を非水溶液中に溶解させた有機電解液が用いられている。しかし、有機電解質では液状であるため、電池が破損したり、過充電時の発熱などにより気化し、常に爆発の危険が伴い、そのために充分な安全策を講じる必要があり、それがまた電池のコストの上昇の原因や使い勝手の悪さになっていた。

【0003】これに対し、最近では無機固体電解質や高分子固体電解質等が多く提案されている。特に、高分子固体電解質では、比較的高いイオン伝導性、広い電位窓、良好な薄膜形成性、柔軟性、軽量性、弾性、透明性等を備えた優れた特徴を持っている。また、2次電池では、多くの電極活性物質が作動中のその体積を変化させるので、高分子固体電解質の柔軟性や弾性的特性は特に重要である。

【0004】このような高分子固体電解質として、特開平8-78053号公報ではシリコーン系化合物が提案されている。しかし、このシリコーン化合物では、十分なイオン伝導性を得られず、実際に電池として使用する場合には有機溶媒等の可塑剤の添加が不可欠である。一方で、このような可塑剤を添加すると機械的強度が低下し、電解質からの液漏れ等が再び問題となってしまう。

【0005】電解質の機械的強度を低下させず、かつに十分なイオン伝導性を得ようとする試みは、米国特許第5,609,974号明細書に記載されている。この特許によれば、架橋されたラジカル重合による高分子により機械的強度や溶媒との親和性等が改良されたとある。しかし、このようなラジカル重合性のポリマーでは、主鎖は炭素間での結合であり、イオン伝導性には寄与しない。このため、架橋によって機械的強度を増大させるといふ試みは、電解質のイオン伝導性を低下させてしまうという欠点を持っていた。

【0006】

【発明が解決しようとする課題】本発明の課題は、高いイオン伝導性を有し、立体架橋構造によって機械的強度を増した繰り返し特性の優れたリチウム2次電池用高分子固体電解質を提供することにある。更には、これを用いて、より低コストでリチウム2次電池を提供することにある。

【0007】

【問題を解決するための手段】本発明者らは鋭意検討した結果、少なくともアルコキシ変性ジアルキルポリシロキサンとポリアルキレンオキサイドとが複合された高分子材料を含有するリチウム2次電池用電解質を用いて上記問題を解決した。更に、このリチウム2次電池用電解質を不織布に含浸してゲル化させた後、正極及び負極材間に担持させることによって、より低コストのリチウム2次電池を提供できることを見出した。

【0008】

【発明の実施の形態】以下、本発明のリチウム2次電池用電解質におけるアルコキシ変性ジアルキルポリシロキサンとポリアルキレンオキサイドとの複合物等の構成物を説明し、続いてこれらを用いたリチウム2次電池の製造方法を説明する。

【0009】本発明のリチウム2次電池用電解質は、少なくともアルコキシ変性ジアルキルポリシロキサンとポリアルキレンオキサイドとの複合物を含有する。本発明に係わるアルコキシ変性ジアルキルポリシロキサンとポリアルキレンオキサイドとの複合物は、アルコキシ変性ジアルキルポリシロキサンとポリアルキレンオキサイドとが複合された高分子材料を意味し、主鎖を構成するポリシロキサン鎖に対してポリアルキレンオキサイドが側鎖にペンダント状に結合している複合材料、または主鎖を構成するポリシロキサン鎖の片末端あるいは両末端にポリアルキレンオキサイドが結合している複合材料、更にはポリシロキサンとポリアルキレンオキサイドがブロック状に結合している複合材料であって、いずれもポリシロキサン鎖の珪素に結合しているアルキル基のうちの一部分がアルコキシ変性を受けている複合材料である。

【0010】アルコキシ変性ジアルキルポリシロキサンとポリアルキレンオキサイドとの複合物の製造方法としては、まずジクロロメチルシラン、ジクロロジメチルシラン及びジクロロメチルメトキシシランの混合物を加水分解させ重合させてポリシロキサン鎖を形成させる。次に、得られたポリシロキサン鎖の珪素に残留する水素とポリエチレンオキサイド $\text{FCH}_2=\text{CHCH}_2\text{O}(\text{CH}_2\text{CH}_2\text{O})_n\text{R}$ （ここでRはアルキル基、nは正の整数を示す）を白金触媒中で反応させて、側鎖にポリエチレンオキサイドを付加させる。

【0011】この時、反応のいずれかの段階でクロルトリメチルシランを併用することによってポリシロキサン鎖の末端のヒドロキシ基を除き、上記複合物を得ること

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ができる。得られた複合物は、加温等の条件下で、ポリシロキサン鎖に結合するメトキシ基を加水分解することによって、架橋することができる。

【0012】更に別の方法としては、ジクロロジメチルシランとジクロロメチルメトキシシランを加水分解させて重合させ、末端にクロルが残存する条件下でポリアルキレンオキサイド $\text{HO}(\text{CH}_2\text{CH}_2\text{O})_m\text{R}'$ （ここで $\text{R}'$ はアルキル基、 $m$ は正の整数を示す）と反応させ、片末端あるいは両末端にポリエチレンオキサイドを付加させて、アルコキシ変性ジアルキルポリシロキサンとポリアルキレンオキサイドとの複合物を得ることができる。

【0013】片末端に付加した場合に残存するヒドロキシ基をクロルトリメチルシランを用いて、反応のいずれかの段階に使用して取り除く必要がある。作製された上記複合物も、メトキシ基を加水分解させることで、架橋することができる。

【0014】このような方法を更に発展させて、ポリシロキサンとポリアルキレンオキサイドの複合前駆体をあらかじめ作製しておき、この前駆体を反応させてブロック型の複合物を得ることができる。

【0015】以上の製造方法では、ポリアルキレンオキサイドとしてポリエチレンオキサイド誘導体を示したが、ポリアルキレンオキサイドとしてはポリエチレンオキサイドの他、ポリプロピレンオキサイドやこれらの混合物及び複合物も使用できる。また、本発明に係わる複合物におけるアルコキシ基としては、出発原料であるジクロロメチルメトキシシランのメトキシ基を他のアルコキシ基に変えることで、メトキシ基だけでなく炭素数3以上のアルコキシ基も導入できるが、反応性の関係からメトキシ基あるいはエトキシ基が好ましい。

【0016】本発明のリチウム2次電池用の電解質を作製する場合には、上述したアルコキシ変性ジアルキルポリシロキサンとポリアルキレンオキサイドの複合物の他に、支持電解質、可塑剤を混合して、不織布に含浸させ加熱等により架橋反応を起こしてゲル化させる。

【0017】本発明で使用する電解質はリチウム塩であり、その具体例としては $\text{LiBPh}$ 、( $\text{Ph}$ はフェニル基を示す)、 $\text{LiBF}_4$ 、 $\text{LiClO}_4$ 、 $\text{LiPF}_6$ 、 $\text{LiAsF}_6$ 、 $\text{LiSbF}_6$ 、 $\text{LiCF}_3\text{SO}_3$ 、 $\text{Li}(\text{CF}_3\text{SO}_2)_2\text{N}$ 、 $\text{LiCF}_3\text{SO}_3$ 、 $\text{Li}(\text{CF}_3\text{SO}_2)_2$ 等のリチウム塩が挙げられるが、特にこれらに限定されるわけではない。これら電解質は、0.1モル/リットル以上8モル/リットルの濃度で使用されるが、0.5モル/リットル以上3.5モル/リットル以下で使用するのが好ましい。

【0018】可塑剤としては非水溶媒が使用でき、その具体例としてはエチレンカーボネイト、プロピレンカーボネイト、ブチレンカーボネイト、ジメチルカーボネイト、ジエチルカーボネイト等のカーボネイト系溶媒、メチラール、1,2-ジメトキシエタン、1,2-ジエ

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キシエタン、1-エトキシ-2-メトキシエタン、アルコキシポリアルキレンエーテル等のエーテル系溶媒、テトラヒドロフラン、2-メチルテトラヒドロフラン、2,5-ジメトキシテトラヒドロフラン等のフラン系溶媒、エチレングリコール、プロピレングリコール、グリセリン、各種ブタンジオール、ポリオキシアルキレングリコール等のアルコール系溶媒等の他、ジオキソラン、ジオキサン等が使用できるが、特にこれらに限定されるわけではない。これらの可塑剤は、2種以上混合して用いることもできる。

【0019】本発明に用いる不織布としては、従来の湿式あるいは乾式のいずれにおいて製造されたものも用いることができるが、アルコキシ変性ジアルキルポリシロキサンとポリアルキレンオキサイドの複合物と可塑剤及び電解質とを混合して得られる電解質溶液のイオン伝導性に対して低抵抗性であり、かつ電解質溶液の保持性に優れた不織布が好適に使用される。不織布に用いられる繊維材としては、ポリエステル、ポリプロピレン、ポリエチレン、テフロン等及びこれらの混合物が挙げられるが、特にこれらに限定されるわけではない。また、その目付量は $100\text{ g/m}^2$ 以下が好ましく、好ましくは $5\sim 50\text{ g/m}^2$ である。使用される繊維材としては、ポリエステル、ポリプロピレン、ポリエチレン、テフロン等であるが特にこれらに限定される訳ではない。

【0020】本発明では、電解質溶液を不織布に含浸した後、加熱等によりアルコキシ変性ジアルキルポリシロキサンとポリアルキレンオキサイドの複合物を架橋させて電解質溶液をゲル化させる。架橋時の加熱温度としては、 $60^\circ\text{C}$ 以上 $250^\circ\text{C}$ 以下が好ましく、より好ましくは $80^\circ\text{C}$ から $180^\circ\text{C}$ 程度に加熱される。

【0021】加熱によりゲル化した電解質溶液はフィルム状となり、この後負極、正極間に保持させてリチウム2次電池となる。負極材としては、リチウム金属、リチウムを含有する炭素材料等が使用できる。正極材としては、金属酸化物、金属硫化物のリチウム複合物、導電性高分子と含硫黄化合物のリチウム複合物等が使用できる。本発明に係わるリチウム2次電池は、コイン、シート、円筒等種々の形態で用いることができる。

【0022】

【作用】本発明は、リチウム2次電池用電解質及びこれを用いたリチウム2次電池の製造方法に関するものであり、少なくともアルコキシ変性ジアルキルポリシロキサンとポリアルキレンオキサイドが複合物を含有することを特徴としている。このアルコキシ変性ジアルキルポリシロキサンとポリアルキレンオキサイドが複合物を含有するリチウム2次電池用電解質は、優れたイオン伝導性を有するばかりでなく、アルコキシ変性ジアルキルポリシロキサン鎖におけるアルコキシ基の反応による立体架橋構造によって、機械的特性の良好なリチウム2次電池用電解質を得ることができる。

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【0023】更に、このリチウム2次電池用電解質不織布に含浸されゲル化した後、正極及び負極材間に担持されることによって、低コストで良好な特性を有するリチウム2次電池を提供することができる。

【0024】

【実施例】以下、実施例により更に本発明を詳細に説明するが、本発明の主旨を越えない限り、これらに限定されるものではない。

【0025】実施例

アルコキシ変性ジアルキルポリシロキサンとポリアルキレンオキサイドの複合物として、メトキシ変性を受けたポリジメチルシロキサンとポリエチレンオキサイド及びポリプロピレンオキサイドがブロック状に配置した分子

量6000の複合物(a)50重量部と、エチレンカーボネイト50重量部、エタノール50重量部、 $\text{LiClO}_4$ を100重量部(約1モル/リットル)をよく混合した。

【0026】この混合液をポリプロピレンの繊維よりなる目付量40g/m<sup>2</sup>の不織布に含浸させ、80℃において30分予備乾燥を行ってエタノールを除去した。更に、120℃で2時間加熱して、総重量80g/m<sup>2</sup>のフィルム状の高分子電解質を作製した。このフィルム状の高分子電解質の電気伝導性を測定したところ、 $2.9 \times 10^{-3} \Omega \text{cm}$ (測定温度23℃)であった。

【0027】負極材としてリチウム金属薄、正極材として $\text{LiCoO}_2$ 87重量部、導電助剤であるアセチレンブラック10重量部、及びバインダーであるポリフッ化ビニリデン3重量部をN-メチル-2-ピロリドン30

重量部と共に十分に混練した混合物を用いた。次に、正負極材間に上記で作製した高分子電解質を担持し、リチウム2次電池を作製した。

【0028】得られたリチウム2次電池の電池特性を検討したところ、この電池は400mAhの容量持ち、1/2CmAでの充放電で容量が80%になるまでのサイクル特性は400回であった。

【0029】比較例

ジアルキルポリシロキサンとポリアルキレンオキサイドの化合物として、ポリジメチルシロキサンが主鎖に、ポリエチレンオキサイドが側鎖に配置した分子量8000の化合物(a)50重量部と、エチレンカーボネイト50重量部、エタノール50重量部、 $\text{LiClO}_4$ を100重量部(約1モル/リットル)をよく混合した。

【0030】この混合液をポリプロピレンの繊維よりなる目付量40g/m<sup>2</sup>の不織布に含浸し、80℃において30分予備乾燥を行ってエタノールを除去した。更に、120℃に2時間加熱したが、電解質はフィルム状とはならず、不織布が電解質を保持できないため、電気伝導性は測定できなかった。

【0031】

【発明の効果】以上説明したとおり、本発明によれば、優れたイオン伝導性を有し、機械的性質の良好なリチウム2次電池用電解質を得ることができる。更に、リチウム2次電池用電解質を不織布に含浸させてゲル化させた後、正極及び負極材間に保持させることによって、低コストで良好な特性を有するリチウム2次電池を提供することができる。

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CLAIMS

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[Claim(s)]

[Claim 1] The electrolyte for lithium rechargeable batteries which carries out the feature of containing the composite of an alkoxy denaturation dialkyl polysiloxane and polyalkylene oxide at least.

[Claim 2] The manufacture method of the lithium rechargeable battery characterized by making it support between positive-electrode and negative-electrode material after sinking into a nonwoven fabric and making it gel the electrolyte for lithium rechargeable batteries in a claim 1.

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DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] This invention relates to the manufacture method of the electrolyte for lithium rechargeable batteries, and also a lithium rechargeable battery.

[0002]

[Description of the Prior Art] A lithium rechargeable battery has a high theoretical energy density, and the application ranges including a portable electronic equipment power supply, such as an electric vehicle and a power supply for power storage, are wide. Since the high solution system of ionic conductivity cannot be used for the electrolyte used for the conventional lithium rechargeable battery because of reactivity with an expensive lithium, the organic electrolytic solution which dissolved lithium salt into the nonaqueous solution is used. However, in the organic electrolyte, since it was liquefied, the cell needed to be damaged, or it needed to evaporate by generation of heat at the time of overcharge etc., the risk of explosion always needed to follow, edfety sufficient for the reason needed to be devised, and it had become the cause of a rise of the cost of a cell, and the badness of user-friendliness again.

[0003] On the other hand, recently, many inorganic solid electrolytes, solid polymer electrolytes, etc. are proposed. Especially, in the solid polymer electrolyte, it has the outstanding feature equipped with comparatively high ion conductivity, a large potential window, good thin film formation nature, flexibility, lightweight nature, elasticity, transparency, etc. Moreover, in a rechargeable battery, since the volume while many electrode active materials are operating is changed, especially the flexibility and the elastic property of a solid polymer electrolyte are important.

[0004] As such a solid polymer electrolyte, the silicone system compound is proposed by JP,8-78053,A. However, in this silicon compound, when sufficient ion conductivity cannot be obtained but it actually uses it as a cell, addition of plasticizers, such as an organic solvent, is indispensable. On the other hand, if such a plasticizer is added, a mechanical strength will fall, and the liquid spill from an electrolyte etc. will pose a problem again.

[0005] the attempt which an electrolytic mechanical strength does not tend to be reduced, and is going to boil it and is going to obtain sufficient ion conductivity is indicated by the U.S. Pat. No. 5,609,974 specification According to this patent, it is that a mechanical strength, compatibility with a solvent, etc. were improved by the macromolecule by the radical polymerization over which the bridge was constructed. However, in the polymer of such radical polymerization nature, a principal chain is combination between carbon and does not contribute to ion conductivity. For this reason, the attempt in which a mechanical strength is increased according to bridge formation had the fault of reducing electrolytic ion conductivity.

[0006]

[Problem(s) to be Solved by the Invention] The technical problem of this invention has high ion conductivity, and is to offer the solid polymer electrolyte for lithium rechargeable batteries which increased the mechanical strength by the solid structure of cross linkage and which was repeatedly

excellent in the property. Furthermore, it is in offering a lithium rechargeable battery by the low cost more using this.

[0007]

[Means for Solving the Problem] This invention persons solved the above-mentioned problem using the electrolyte for lithium rechargeable batteries containing the polymeric materials with which an alkoxy denaturation dialkyl polysiloxane and polyalkylene oxide were compounded at least, as a result of inquiring wholeheartedly. Furthermore, after sinking into the nonwoven fabric and making it gel this electrolyte for lithium rechargeable batteries, it found out that the lithium rechargeable battery of a low cost could be offered more by making it support between positive-electrode and negative-electrode material.

[0008]

[Embodiments of the Invention] Hereafter, structures, such as a composite of the alkoxy denaturation dialkyl polysiloxane and polyalkylene oxide in the electrolyte for lithium rechargeable batteries of this invention, are explained, and the manufacture method of a lithium rechargeable battery using these is explained continuously.

[0009] The electrolyte for lithium rechargeable batteries of this invention contains the composite of an alkoxy denaturation dialkyl polysiloxane and polyalkylene oxide at least. The composite of the alkoxy denaturation dialkyl polysiloxane and polyalkylene oxide concerning this invention The polymeric materials with which an alkoxy denaturation dialkyl polysiloxane and polyalkylene oxide were compounded are meant. The composite material which polyalkylene oxide has combined with the side chain in the shape of a pendant to the polysiloxane chain which constitutes a principal chain, Or the composite material which polyalkylene oxide has combined with the piece end or both ends of a polysiloxane chain which constitutes a principal chain, Furthermore, a polysiloxane and polyalkylene oxide are the composite material combined in the shape of a block, and the part of the alkyl groups which have combined all with the silicon of a polysiloxane chain is the composite material which has received alkoxy denaturation.

[0010] As the manufacture method of the composite of an alkoxy denaturation dialkyl polysiloxane and polyalkylene oxide, the mixture of a dichloro methylsilane, dichloro dimethylsilane, and a dichloro methyl methoxy silane is made to understand an added water part first, a polymerization is carried out, and a polysiloxane chain is made to form. Next, the hydrogen and polyethylene-oxide  $\text{CH}_2=\text{CHCH}_2\text{O}(\text{CH}_2\text{CH}_2\text{O})_n\text{R}$  (R shows an alkyl group and n shows a positive integer here) which remain to the silicon of the obtained polysiloxane chain are made to react in a platinum catalyst, and a polyethylene oxide is made to add to a side chain.

[0011] At this time, the above-mentioned composite can be obtained except for the hydroxy group of the end of a polysiloxane chain by using a crawl trimethyl silane together in one stage of the reactions. The obtained composite can construct a bridge by understanding the methoxy machine combined with a polysiloxane chain an added water part under conditions, such as warming.

[0012] Furthermore, it can be made to be able to react with polyalkylene oxide  $\text{HO}(\text{CH}_2\text{CH}_2\text{O})_m\text{R}'$  (for R' to show an alkyl group and for m to show a positive integer here) on the conditions to which dichloro dimethylsilane and a dichloro methyl methoxy silane are made to understand an added water part, a polymerization is carried out as an option, and the crawl remains at the end, a polyethylene oxide can be made to be able to add to a piece end or both ends, and the composite of a

[0013] It is necessary using a crawl trimethyl silane to use the hydroxy group which remains when it adds to a piece end for one stage of the reactions, and to remove it. The produced above-mentioned composite can also construct a bridge by making a methoxy machine understand an added water part.

[0014] Such a method is developed further, the compound precursor of a polysiloxane and polyalkylene oxide is produced beforehand, this precursor can be made to be able to react and the composite of a block type can be obtained.

[0015] By the above manufacture method, although the polyethylene-oxide derivative was shown as polyalkylene oxide, as polyalkylene oxide, others and polypropylene oxide, and these mixture and



composites can also be used. [ polyethylene oxide ] Moreover, although it is changing into other alkoxy groups the methoxy machine of the dichloro methyl methoxy silane which is a start raw material as an alkoxy group in the composite concerning this invention and not only a methoxy machine but a three or more-carbon number alkoxy group can be introduced, the reactant methoxy machine from a relation or a reactant ethoxy basis is desirable.

[0016] When producing the electrolyte for the lithium rechargeable batteries of this invention, a nonwoven fabric is infiltrated, and crosslinking reaction is caused by heating etc. and it is made to mix the supporting electrolyte and plasticizer other than the composite of an alkoxy denaturation dialkyl polysiloxane and polyalkylene oxide which were mentioned above, and to gel.

[0017] The electrolyte used by this invention is not necessarily limited to especially these, although it is lithium salt and the lithium salt of LiBPh<sub>4</sub> (Ph shows a phenyl group), LiBF<sub>4</sub>, LiClO<sub>4</sub>, LiPF<sub>6</sub>, LiAsF<sub>6</sub>, LiSbF<sub>6</sub>, LiCF<sub>3</sub>SO<sub>3</sub>, Li(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N, LiCF<sub>3</sub>SO<sub>3</sub>, and LiC(CF<sub>3</sub>SO<sub>2</sub>)<sub>3</sub> grade is mentioned as the example. Although these electrolytes are used by the concentration of 0.1 mols/l. or more eight mols/l., it is desirable to use it by 1. in 0.5 mols/l. or more 3.5 mols /or less.

[0018] A non-aqueous solvent can be used as a plasticizer. as the concrete RE Ethylene carbonate, Propylene carbonate, butylene carbonate, dimethyl carbonate, Carbonate system solvents, such as diethyl carbonate, a methylal, 1, 2-dimethoxyethane, Ether system solvents, such as 1, 2-diethoxy ethane, 1-ethoxy-2-methoxyethane, and the alkoxy polyalkylene ether, Furan system solvents, such as tetrahydrofuran, 2-methyl tetrahydrofuran, 2, and 5-dimethoxy tetrahydrofuran, Although a dioxolane besides being alcoholic system solvents, such as ethylene glycol, a propylene glycol, a glycerol, various butanediol, and polyoxy alkylene glycol, etc., a dioxane, etc. can be used, it is not necessarily limited to especially these. Two or more sorts can be mixed and these plasticizers can also be used.

[0019] Although what was manufactured in wet [ conventional ] or dry-type any as a nonwoven fabric used for this invention can be used, the nonwoven fabric which is low resistance and was excellent in the maintenance nature of an electrolytic solution to the ion conductivity of the electrolytic solution which mixes the composite, plasticizer, and electrolyte of an alkoxy denaturation dialkyl polysiloxane and polyalkylene oxide, and is obtained is used suitably. As a fiber material used for a nonwoven fabric, although such mixture, such as polyester, polypropylene, polyethylene, and Teflon, is mentioned, it is not necessarily limited to especially these. Moreover, the amount of eyes has two or less desirable 100 g/m, and it is 5 - 50 g/m<sup>2</sup> preferably. As a fiber material used, especially although it is polyester, polypropylene, polyethylene, Teflon, etc., it is not necessarily limited to these.

[0020] After sinking an electrolytic solution into a nonwoven fabric, the composite of an alkoxy denaturation dialkyl polysiloxane and polyalkylene oxide is made to construct a bridge by heating etc., and an electrolytic solution is made to gel in this invention. As heating temperature at the time of bridge formation, 60 degrees C or more 250 degrees C or less are desirable, and is more preferably heated from 80 degrees C to about 180 degrees C.

[0021] The electrolytic solution gelled by heating becomes film-like, is made to hold between a negative electrode and a positive electrode after this, and serves as a lithium rechargeable battery. As negative-electrode material, the carbon material containing a lithium metal and a lithium etc. can be used. As positive-electrode material, a metallic oxide, the lithium composite of metallic sulfide, the lithium composite of a conductive polymer and a sulphur-containing compound, etc. can be used. The lithium rechargeable battery concerning this invention can be used with various forms, such as coin, a sheet, and a cylinder.

[0022]

[Function] this invention is characterized by an alkoxy denaturation dialkyl polysiloxane and polyalkylene oxide containing a composite at least about the manufacture method of the lithium rechargeable battery which used the electrolyte for lithium rechargeable batteries, and this. The electrolyte for lithium rechargeable batteries with which this alkoxy denaturation dialkyl polysiloxane and polyalkylene oxide contain a composite not only has the outstanding ion conductivity, but can

obtain the good electrolyte for lithium rechargeable batteries of a mechanical property by the solid structure of cross linkage by the reaction of the alkoxy group in an alkoxy denaturation dialkyl polysiloxane chain.

[0023] Furthermore, after sinking into this electrolyte nonwoven fabric for lithium rechargeable batteries and gelling, the lithium rechargeable battery which has a good property by the low cost can be offered by being supported between positive-electrode and negative-electrode material.

[0024]

[Example] Hereafter, although an example explains this invention in detail further, unless the main point of this invention is exceeded, it is not limited to these.

[0025] An example alkoxy denaturation dialkyl polysiloxane, the poly dimethylsiloxane which received methoxy denaturation as a composite of polyalkylene oxide, a polyethylene oxide, and polypropylene oxide often mixed the 100 weight sections (about one mol/(l.)) for the (Composite a) 50 weight section of the molecular weight 6000 arranged in the shape of a block, the ethylene carbonate 50 weight section and the ethanol 50 weight section, and  $\text{LiClO}_4$ .

[0026] This mixed liquor was infiltrated into the nonwoven fabric of amount of eyes 40 g/m<sup>2</sup> which consists of fiber of polypropylene, predrying was performed in 80 degrees C for 30 minutes, and ethanol was removed. Furthermore, it heated at 120 degrees C for 2 hours, and the polyelectrolyte of the shape of a film of AUW 80 g/m<sup>2</sup> was produced. When the electrical conductivity of the polyelectrolyte of the shape of this film was measured, it was  $2.9 \times 10^3$ -ohmcm (measurement temperature of 23 degrees C).

[0027] The mixture which fully kneaded the  $\text{LiCoO}_2$  87 weight section, the acetylene black 10 weight section which is an electric conduction assistant, and the polyvinylidene-fluoride 3 weight section which is a binder with the N-methyl-2-pyrrolidone 30 weight section was used as lithium \*\*\*\*\* and positive-electrode material as negative-electrode material. Next, between positive/negative pole material, the polyelectrolyte produced above was supported and the lithium rechargeable battery was produced.

[0028] When the cell property of the obtained lithium rechargeable battery was examined, the cycle property until, as for this cell, capacity becomes 80% by capacity \*\*\*\* of 400mAh(s) and the charge and discharge in 1/2CmA was 400 times.

[0029] As a compound of the example dialkyl polysiloxane of comparison, and polyalkylene oxide, the 100 weight sections (about one mol/(l.)) were often mixed for the (Compound a) 50 weight section of the molecular weight 8000 which poly dimethylsiloxane has arranged to the principal chain and the polyethylene oxide has arranged to the side chain, the ethylene carbonate 50 weight section and the ethanol 50 weight section, and  $\text{LiClO}_4$ .

[0030] It sank into the nonwoven fabric of amount of eyes 40 g/m<sup>2</sup> which consists this mixed liquor of fiber of polypropylene, predrying was performed in 80 degrees C for 30 minutes, and ethanol was removed. Furthermore, although heated at 120 degrees C for 2 hours, since an electrolyte did not become film-like and a nonwoven fabric was not able to hold an electrolyte, electrical conductivity has not been measured.

[0031]

[Effect of the Invention] According to this invention, it has the outstanding ion conductivity and the good electrolyte for lithium rechargeable batteries of a mechanical property can be obtained as explained above. Furthermore, after infiltrating a nonwoven fabric and making the electrolyte for lithium rechargeable batteries gel, the lithium rechargeable battery which has a good property by the low cost can be offered by making it hold between positive-electrode and negative-electrode material.

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TECHNICAL FIELD

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[The technical field to which invention belongs] This invention relates to the manufacture method of the electrolyte for lithium rechargeable batteries, and also a lithium rechargeable battery.

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PRIOR ART

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[Description of the Prior Art] A lithium rechargeable battery has a high theoretical energy density, and the application ranges including a portable electronic equipment power supply, such as an electric vehicle and a power supply for power storage, are wide. Since the high solution system of ionic conductivity cannot be used for the electrolyte used for the conventional lithium rechargeable battery because of reactivity with an expensive lithium, the organic electrolytic solution which dissolved lithium salt into the nonaqueous solution is used. However, in the organic electrolyte, since it was liquefied, the cell needed to be damaged, or it needed to evaporate by generation of heat at the time of overcharge etc., the risk of explosion always needed to follow, edfety sufficient for the reason needed to be devised, and it had become the cause of a rise of the cost of a cell, and the badness of user-friendliness again.

[0003] On the other hand, recently, many inorganic solid electrolytes, solid polymer electrolytes, etc. are proposed. Especially, in the solid polymer electrolyte, it has the outstanding feature equipped with comparatively high ion conductivity, a large potential window, good thin film formation nature, flexibility, lightweight nature, elasticity, transparency, etc. Moreover, in a rechargeable battery, since the volume while many electrode active materials are operating is changed, especially the flexibility and the elastic property of a solid polymer electrolyte are important.

[0004] As such a solid polymer electrolyte, the silicone system compound is proposed by JP,8-78053,A. However, in this silicon compound, when sufficient ion conductivity cannot be obtained but it actually uses it as a cell, addition of plasticizers, such as an organic solvent, is indispensable. On the other hand, if such a plasticizer is added, a mechanical strength will fall, and the liquid spill from an electrolyte etc. will pose a problem again.

[0005] the attempt which an electrolytic mechanical strength does not tend to be reduced, and is going to boil it and is going to obtain sufficient ion conductivity is indicated by the U.S. Pat. No. 5,609,974 specification According to this patent, it is that a mechanical strength, compatibility with a solvent, etc. were improved by the macromolecule by the radical polymerization over which the bridge was constructed. However, in the polymer of such radical polymerization nature, a principal chain is combination between carbon and does not contribute to ion conductivity. For this reason, the attempt in which a mechanical strength is increased according to bridge formation had the fault of reducing electrolytic ion conductivity.

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## EFFECT OF THE INVENTION

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[Effect of the Invention] According to this invention, it has the outstanding ion conductivity and the good electrolyte for lithium rechargeable batteries of a mechanical property can be obtained as explained above. Furthermore, after infiltrating a nonwoven fabric and making the electrolyte for lithium rechargeable batteries gel, the lithium rechargeable battery which has a good property by the low cost can be offered by making it hold between positive-electrode and negative-electrode material.

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TECHNICAL PROBLEM

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[Problem(s) to be Solved by the Invention] The technical problem of this invention has high ion conductivity, and is to offer the solid polymer electrolyte for lithium rechargeable batteries which increased the mechanical strength by the solid structure of cross linkage and which was repeatedly excellent in the property. Furthermore, it is in offering a lithium rechargeable battery by the low cost more using this.

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MEANS

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[Means for Solving the Problem] This invention persons solved the above-mentioned problem using the electrolyte for lithium rechargeable batteries containing the polymeric materials with which an alkoxy denaturation dialkyl polysiloxane and polyalkylene oxide were compounded at least, as a result of inquiring wholeheartedly. Furthermore, after sinking into the nonwoven fabric and making it gel this electrolyte for lithium rechargeable batteries, it found out that the lithium rechargeable battery of a low cost could be offered more by making it support between positive-electrode and negative-electrode material.

[0008]

[Embodiments of the Invention] Hereafter, structures, such as a composite of the alkoxy denaturation dialkyl polysiloxane and polyalkylene oxide in the electrolyte for lithium rechargeable batteries of this invention, are explained, and the manufacture method of a lithium rechargeable battery using these is explained continuously.

[0009] The electrolyte for lithium rechargeable batteries of this invention contains the composite of an alkoxy denaturation dialkyl polysiloxane and polyalkylene oxide at least. The composite of the alkoxy denaturation dialkyl polysiloxane and polyalkylene oxide concerning this invention, The polymeric materials with which an alkoxy denaturation dialkyl polysiloxane and polyalkylene oxide were compounded are meant. The composite material which polyalkylene oxide has combined with the side chain in the shape of a pendant to the polysiloxane chain which constitutes a principal chain, Or the composite material which polyalkylene oxide has combined with the piece end or both ends of a polysiloxane chain which constitutes a principal chain, Furthermore, a polysiloxane and polyalkylene oxide are the composite material combined in the shape of a block, and the part of the alkyl groups which have combined all with the silicon of a polysiloxane chain is the composite material which has received alkoxy denaturation.

[0010] As the manufacture method of the composite of an alkoxy denaturation dialkyl polysiloxane and polyalkylene oxide, the mixture of a dichloro methylsilane, dichloro dimethylsilane, and a dichloro methyl methoxy silane is made to understand an added water part first, a polymerization is carried out, and a polysiloxane chain is made to form. Next, the hydrogen and polyethylene-oxide  $\text{CH}_2=\text{CHCH}_2\text{O}(\text{CH}_2\text{CH}_2\text{O})_n\text{R}$  (R shows an alkyl group and n shows a positive integer here) which remain to the silicon of the obtained polysiloxane chain are made to react in a platinum catalyst, and a polyethylene oxide is made to add to a side chain.

[0011] At this time, the above-mentioned composite can be obtained except for the hydroxy group of the end of a polysiloxane chain by using a crawl trimethyl silane together in one stage of the reactions. The obtained composite can construct a bridge by understanding the methoxy machine combined with a polysiloxane chain an added water part under conditions, such as warming.

[0012] Furthermore, it can be made to be able to react with polyalkylene oxide  $\text{HO}(\text{CH}_2\text{CH}_2\text{O})_m\text{R}'$  (for R' to show an alkyl group and for m to show a positive integer here) on the conditions to which dichloro dimethylsilane and a dichloro methyl methoxy silane are made to understand an added water part, a polymerization is carried out as an option, and the crawl remains at the end, a polyethylene oxide can be made to be able to add to a piece end or both ends, and the composite of a

[0013] It is necessary using a crawl trimethyl silane to use the hydroxy group which remains when it adds to a piece end for one stage of the reactions, and to remove it. The produced above-mentioned composite can also construct a bridge by making a methoxy machine understand an added water part.



[0014] Such a method is developed further, the compound precursor of a polysiloxane and polyalkylene oxide is produced beforehand, this precursor can be made to be able to react and the composite of a block type can be obtained.

[0015] By the above manufacture method, although the polyethylene-oxide derivative was shown as polyalkylene oxide, as polyalkylene oxide, others and polypropylene oxide, and these mixture and composites can also be used. [ polyethylene oxide ] Moreover, although it is changing into other alkoxy groups the methoxy machine of the dichloro methyl methoxy silane which is a start raw material as an alkoxy group in the composite concerning this invention and not only a methoxy machine but a three or more-carbon number alkoxy group can be introduced, the reactant methoxy machine from a relation or a reactant ethoxy basis is desirable.

[0016] When producing the electrolyte for the lithium rechargeable batteries of this invention, a nonwoven fabric is infiltrated, and crosslinking reaction is caused by heating etc. and it is made to mix the supporting electrolyte and plasticizer other than the composite of an alkoxy denaturation dialkyl polysiloxane and polyalkylene oxide which were mentioned above, and to gel.

[0017] The electrolyte used by this invention is not necessarily limited to especially these, although it is lithium salt and the lithium salt of LiBPh<sub>4</sub> (Ph shows a phenyl group), LiBF<sub>4</sub>, LiClO<sub>4</sub>, LiPF<sub>6</sub>, LiAsF<sub>6</sub>, LiSbF<sub>6</sub>, LiCF<sub>3</sub>SO<sub>3</sub>, Li(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N, LiCF<sub>3</sub>SO<sub>3</sub>, and LiC(CF<sub>3</sub>SO<sub>2</sub>)<sub>3</sub> grade is mentioned as the example. Although these electrolytes are used by the concentration of 0.1 mols/l. or more eight mols/l., it is desirable to use it by 1. in 0.5 mols/l. or more 3.5 mols /or less.

[0018] A non-aqueous solvent can be used as a plasticizer. as the concrete RE Ethylene carbonate, Propylene carbonate, butylene carbonate, dimethyl carbonate, Carbonate system solvents, such as diethyl carbonate, a methylal, 1, 2-dimethoxyethane, Ether system solvents, such as 1, 2-diethoxy ethane, 1-ethoxy-2-methoxyethane, and the alkoxy polyalkylene ether, Furan system solvents, such as tetrahydrofuran, 2-methyl tetrahydrofuran, 2, and 5-dimethoxy tetrahydrofuran, Although a dioxolane besides being alcoholic system solvents, such as ethylene glycol, a propylene glycol, a glycerol, various butanediol, and polyoxy alkylene glycol, etc., a dioxane, etc. can be used It is not necessarily limited to especially these. Two or more sorts can be mixed and these plasticizers can also be used.

[0019] Although what was manufactured in wet [ conventional ] or dry-type any as a nonwoven fabric used for this invention can be used, the nonwoven fabric which is low resistance and was excellent in the retentivity of an electrolytic solution to the ion conductivity of the electrolytic solution which mixes the composite, plasticizer, and electrolyte of an alkoxy denaturation dialkyl polysiloxane and polyalkylene oxide, and is obtained is used suitably. As a fiber material used for a nonwoven fabric, although such mixture, such as polyester, polypropylene, polyethylene, and Teflon, is mentioned, it is not necessarily limited to especially these. Moreover, the amount of eyes has two or less desirable 100 g/m, and it is 5 - 50 g/m<sup>2</sup> preferably. As a fiber material used, especially although it is polyester, polypropylene, polyethylene, Teflon, etc., it is not necessarily limited to these.

[0020] After sinking an electrolytic solution into a nonwoven fabric, the composite of an alkoxy denaturation dialkyl polysiloxane and polyalkylene oxide is made to construct a bridge by heating etc., and an electrolytic solution is made to gel in this invention. As heating temperature at the time of bridge formation, 60 degrees C or more 250 degrees C or less are desirable, and is more preferably heated from 80 degrees C to about 180 degrees C.

[0021] The electrolytic solution gelled by heating becomes film-like, is made to hold between a negative electrode and a positive electrode after this, and serves as a lithium rechargeable battery. As negative-electrode material, the carbon material containing a lithium metal and a lithium etc. can be used. As positive-electrode material, a metallic oxide, the lithium composite of metallic sulfide, the lithium composite of a conductive polymer and a sulphur-containing compound, etc. can be used. The lithium rechargeable battery concerning this invention can be used with various gestalten, such as coin, a sheet, and a cylinder.

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## OPERATION

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[Function] this invention is characterized by an alkoxy denaturation dialkyl polysiloxane and polyalkylene oxide containing a composite at least about the manufacture method of the lithium rechargeable battery which used the electrolyte for lithium rechargeable batteries, and this. The electrolyte for lithium rechargeable batteries with which this alkoxy denaturation dialkyl polysiloxane and polyalkylene oxide contain a composite not only has the outstanding ion conductivity, but can obtain the good electrolyte for lithium rechargeable batteries of a mechanical property by the solid structure of cross linkage by the reaction of the alkoxy group in an alkoxy denaturation dialkyl polysiloxane chain.

[0023] Furthermore, after sinking into this electrolyte nonwoven fabric for lithium rechargeable batteries and gelling, the lithium rechargeable battery which has a good property by the low cost can be offered by being supported between positive-electrode and negative-electrode material.

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EXAMPLE

[Example] Hereafter, although an example explains this invention in detail further, unless the main point of this invention is exceeded, it is not limited to these.

[0025] An example alkoxy denaturation dialkyl polysiloxane, the poly dimethylsiloxane which received methoxy denaturation as a composite of polyalkylene oxide, a polyethylene oxide, and polypropylene oxide often mixed the 100 weight sections (about one mol/(l.)) for the (Composite a) 50 weight section of the molecular weight 6000 arranged in the shape of a block, the ethylene carbonate 50 weight section and the ethanol 50 weight section, and LiClO<sub>4</sub>.

[0026] This mixed liquor was infiltrated into the nonwoven fabric of amount of eyes 40 g/m<sup>2</sup> which consists of fiber of polypropylene, predrying was performed in 80 degrees C for 30 minutes, and ethanol was removed. Furthermore, it heated at 120 degrees C for 2 hours, and the polyelectrolyte of the shape of a film of AUW 80 g/m<sup>2</sup> was produced. When the electrical conductivity of the polyelectrolyte of the shape of this film was measured, it was 2.9x10<sup>3</sup>-ohmcm (measurement temperature of 23 degrees C).

[0027] The mixture which fully kneaded the LiCoO<sub>2</sub> 87 weight section, the acetylene black 10 weight section which is an electric conduction assistant, and the polyvinylidene-fluoride 3 weight section which is a binder with the N-methyl-2-pyrrolidone 30 weight section was used as lithium \*\*\*\*\* and positive-electrode material as negative-electrode material. Next, between positive/negative pole material, the polyelectrolyte produced above was supported and the lithium rechargeable battery was produced.

[0028] When the cell property of the obtained lithium rechargeable battery was examined, the cycle property until, as for this cell, capacity becomes 80% by capacity \*\*\*\* of 400mAh(s) and the charge and discharge in 1/2CmA was 400 times.

[0029] As a compound of the example dialkyl polysiloxane of comparison, and polyalkylene oxide, the 100 weight sections (about one mol/(l.)) were often mixed for the (Compound a) 50 weight section of the molecular weight 8000 which poly dimethylsiloxane has arranged to the principal chain and the polyethylene oxide has arranged to the side chain, the ethylene carbonate 50 weight section and the ethanol 50 weight section, and LiClO<sub>4</sub>.

[0030] It sank into the nonwoven fabric of amount of eyes 40 g/m<sup>2</sup> which consists this mixed liquor of fiber of polypropylene, predrying was performed in 80 degrees C for 30 minutes, and ethanol was removed. Furthermore, although heated at 120 degrees C for 2 hours, since an electrolyte did not become film-like and a nonwoven fabric was not able to hold an electrolyte, electrical conductivity has not been measured.

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